Using Guard Bands to Accommodate Uncertainty in the Spark AES Analysis of Aluminum or Aluminum Alloys When Determining Compliance with Specified Composition limits

Summary

Every pound of aluminum or aluminum alloys cast and sold is certified to meet The Aluminum Association Inc. registered limits or other specified composition limits. Certification of aluminum and aluminum alloys to specified composition limits is typically done using Spark-Atomic Emission Spectrometry (Spark-AES) following the procedures in ASTM International (ASTM) E716 *Standard Practices for Sampling and Sample Preparation of Aluminum and Aluminum Alloys for Determination of Chemical Composition by Spectrochemical Analysis* and ASTM E1251   *Standard Test Method for Analysis of Aluminum and Aluminum Alloys by Spark-AES*. Spark-AES Laboratories at major aluminum production facilities normally have excellent analytical practices and follow strict quality control protocols to provide the best results possible. However, every measurement has an associated uncertainty and the measurement of composition using Spark-AES is no exception to the rule.

This paper provides a brief discussion of:

1. The uncertainty inherent in the elemental analysis of aluminum and aluminum alloys by Spark-AES.
2. The benefits of using guard bands to set internal operating limits, which are offset from specified composition limits.
3. A model of the risk for sale of out-of-specification product based on the analysis uncertainty relative to the specified composition limits.
4. The main sources of uncertainty of Spark-AES and their potential causes.

Scope

The scope of this paper is limited to results obtained by a single lab on cast metal samples taken in accordance with ASTM E716 and analyzed in accordance with ASTM E1251. Analysis by more than one lab may add uncertainty to the measurement process and is not within the scope of this paper.

References

1. ASTM E716 - *Standard Practices for Sampling and Sample Preparation of Aluminum and Aluminum Alloys for Determination of Chemical Composition by Spectrochemical Analysis.*

2. ASTM E 1251 - *Standard Test Method for Analysis of Aluminum and Aluminum Alloys by Spark-AES.*

3. ISO 3534-1:1993. "Statistics - Vocabulary and symbols - Part 1: Probability and general statistical terms".

4. EURACHEM/CITAC Guide: *Use of Uncertainty Information in Compliance Assessment,* First edition 2007, Editors S L R Ellison (LGC, UK), A Williams (UK)

5. ISO/IEC Guide 99 - *International vocabulary of metrology -- Basic and general concepts and associated terms (VIM)*

6. *International Alloy Designations and Chemical Composition Limits for Wrought Aluminum and Wrought Aluminum Alloys* (Teal Sheets)

7. *Designations and Chemical Composition Limits for Aluminum Alloys in the Form of Castings and Ingot* (Pink sheets)

8. *International Designations and Chemical Composition Limits for Unalloyed Aluminum* (Gold Sheets)

9. *ANSI H35.1/H35.1M American National Standard Alloy and Temper Designation Systems for Aluminum*

Terms

Bias – The difference between the average value of the test results and an accepted reference value.

> Note: Bias is the total systematic error as contrasted to random error. There may be one or more systematic error components contributing to the bias. A larger systematic difference from the accepted reference value is reflected by a larger bias value.'

> Note: An accepted reference value comes from either a certified reference material or results from analysis of the product by a method that is accepted as having no bias.

Detection limit, *in analysis* – The minimum single result which, with a stated probability, can be distinguished from a suitable blank value.

Note: The limit defines the point at which the analysis becomes possible, and this may be different from the lower limit of the determinable analytical range.

Note: Detection limit may be estimated by using a fully calibrated method to measure 10 independent sample blanks once each and calculating the mean mass fraction result, $\bar{x}_{bl}$, and its standard deviation, s. $LoD = |\bar{x}_{bl}| + 3s$.

Guard Bands – The differences between internal operating limits and specified composition limits.

Measurement uncertainty - parameter, associated with the result of a measurement, which characterizes the dispersion of the values that could reasonably be attributed to the measurand including random and systematic errors.

Operating Range - Compositions within the internal operating limits, which are inside the specified composition limits.

Furnace composition variability – the distribution of compositions resulting from multiple furnace charges and furnace alloying practices, which include a variety of metal sources, uncertainty in melt weight, temperature variations, and oxidation or volatility considerations.

Introduction

Producers of aluminum or aluminum alloys typically measure composition on 100 % of their cast products by taking samples from the molten metal, in accordance with ASTM E716, and analyzing the samples using Spark Atomic Emission Spectrometry (Spark-AES) according to ASTM E1251. The goal is always to provide accurate quantitative results, but uncertainty occurs in all Spark-AES measurements, even when using properly calibrated instruments and the best possible sampling, sample preparation and analysis procedures.   The inherent uncertainty of the analysis should be considered when establishing and determining compliance with specified composition limits. Under the best of circumstances, two analyses on the same sample will not likely produce the same results, even when using the same instrument. This uncertainty in measuring composition may cause the following problems when the analysis result is close to a specification limit:

1) a false negative outcome, (i.e. a measured composition that is outside the specification limit when the actual composition meets the specification) or
2) a false positive outcome (i.e. a measured composition that meets the specification limit when the actual composition is outside the specification).

When the uncertainty interval of a Spark AES measured result overlaps a specified composition limit, the likelihood for a false positive or a false negative outcome increases, as illustrated in Figures 1 and 2.

The blue curves in Figures 1 and 2 represent the expected frequency distribution of measured Spark AES results, assumed to be normal or Gaussian shaped, around an actual (true) value. Figure 1 illustrates the possibility that a measured result of a sample, having an actual composition above the specified minimum composition limit, is below the specified minimum composition limit due to the inherent uncertainty of the analysis. This illustrates the case of a false negative outcome. Conversely, Figure 2 shows the case of a false positive outcome where a measured result of a sample is above the specified minimum composition limit, but the actual composition is below the specified minimum composition limit.
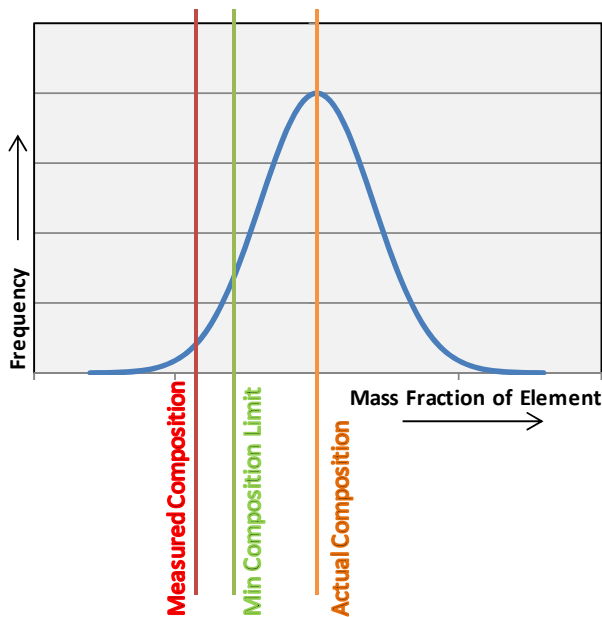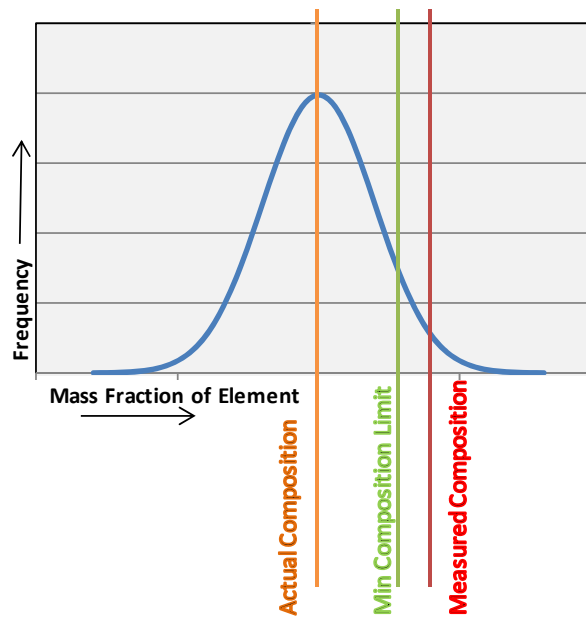
Figure 1. False Negative Outcome

Figure 2. False Positive Outcome

Discussion of Guard Bands

An effective way to accommodate measurement uncertainty is through the use of internal operating limits tighter than the specified composition limits as shown in Figure 3. Assuming

that the furnace composition variability follows a normal distribution centered on the nominal composition of a given alloy specification, the figure shows how the knowledge of measurement uncertainty can be used to select internal operating limits that protect against occurrences of false negative or false positive outcomes. The differences between internal operating limits and specified composition limits are sometimes referred to as *guard bands*. According to Figure 3, product having an analysis result between the internal operating limits would be expected to comply with the specified limits. However, product having an analysis value between the internal limits and the specified composition limits may or may not meet the specified composition limits due to the measurement uncertainty. When establishing practices to ensure compliance with specified composition limits, producers should consider the use of guard bands based on the Spark-AES test method uncertainty.
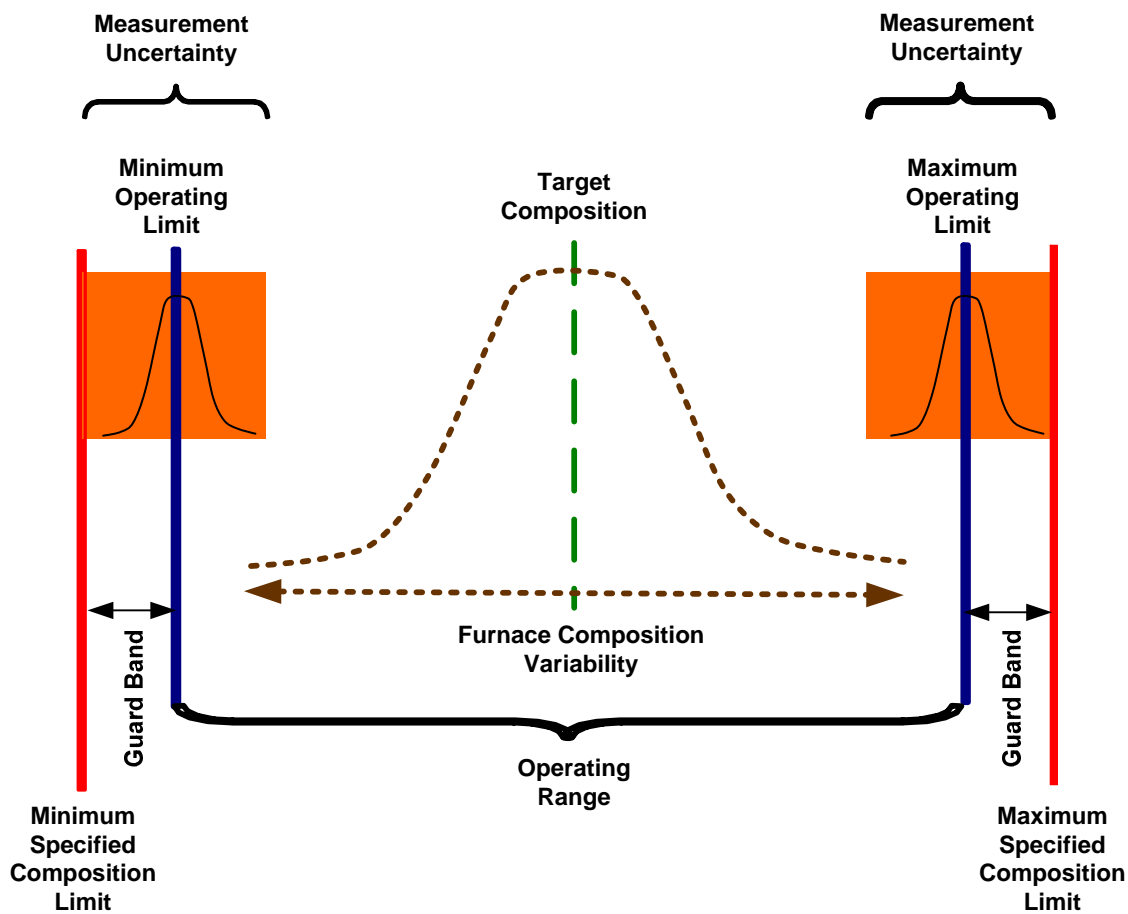

Figure 3 illustrates the case where the specified composition range is wide enough to accommodate both the furnace composition variability and guard bands to account for Spark-AES test method uncertainty. This is the best case scenario for reliably producing product that meets specified composition limits.

Consider the case illustrated in Figure 4 where the specified composition range is wide enough to accommodate guard bands but not wide enough for the operating range to be greater than the furnace composition variability. In this case, the use of guard bands will ensure the product composition is within specified composition limits. However, as the specified composition range becomes tighter, it becomes more difficult and less practical to produce product that reliably meets the specified composition limits without generating excessive internal scrap. Based on the expected furnace composition variability, some amount of product with composition between the specified composition limit and operating limit will be scrapped, which may impact the cost and on-time delivery of the product.
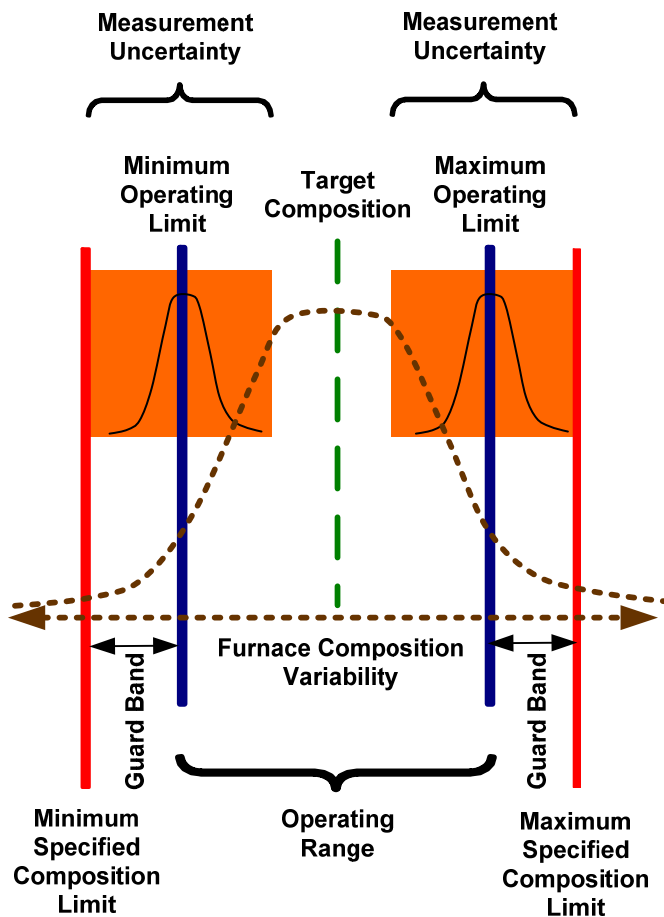

Figure 4 illustrates the effect of a narrow specified composition range relative to the operating range and the furnace composition variability.

In the worst case scenario as illustrated in Figure 5, the specified composition range becomes so narrow that the measurement uncertainty for results close to the operating limits defined by guard bands may overlap, and the furnace composition variability exceeds the specified composition limits. In this case, the use of guard bands and operating limits to account for Spark AES test method uncertainty is impossible, which increases the probability of shipping product that is outside the specified composition

limits. This scenario also results in the production of internal scrap and its attendant impact on cost and delivery.
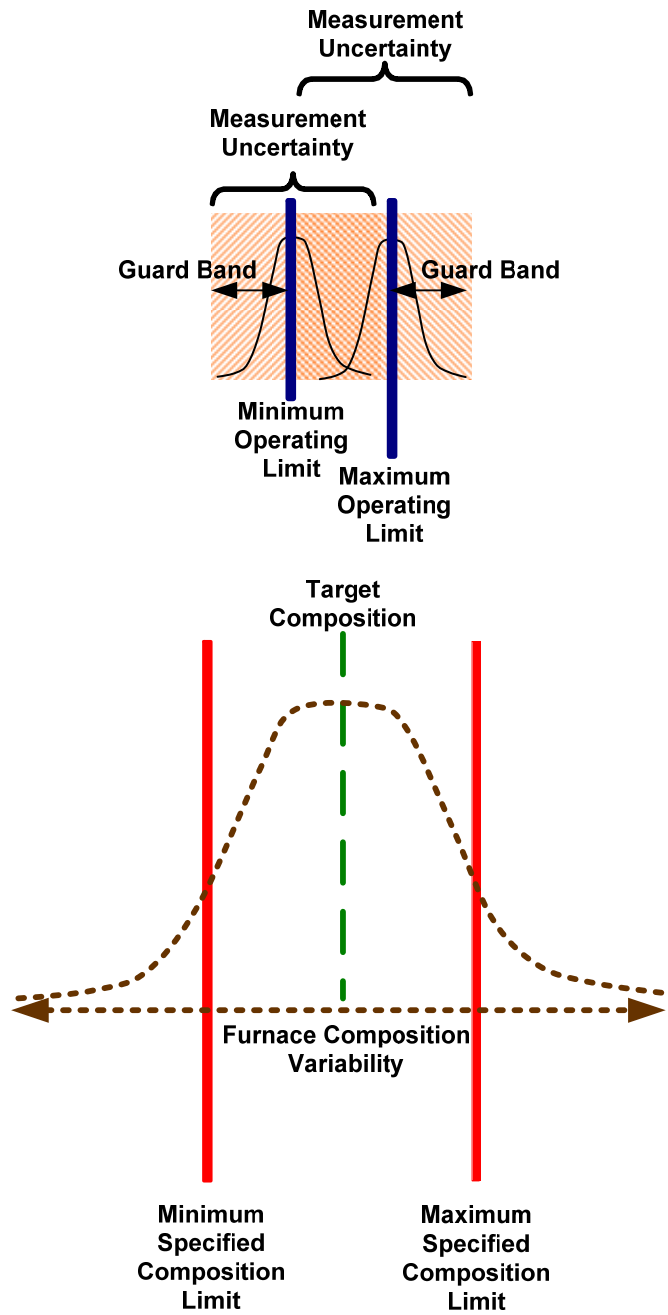

Figure 5 Illustrates the effect of further restricting the specified composition range such that the use of guard bands and operating limits becomes impossible.

Guard Band Examples

Only a detailed analysis of the various sources of uncertainty can provide an accurate estimate of their magnitudes. The magnitude of the uncertainty may vary with concentration and element as shown by the precision and bias data given in Table 3 of ASTM E1251.   Modern instruments often have a short term variation (spark to spark) better than 0.5% relative on good quality certified reference materials (CRM) and 1% relative on homogeneous production samples. Repeatability between sparks on reference materials and samples is only one part of the overall uncertainty of the final composition result. Sampling, sample preparation, certification uncertainty on CRM, drift correction method, type standardization, and instrument drift add to the total uncertainty of the result.   Considering the sources of uncertainty, it is likely that even the best labs have an overall uncertainty of about ± 3% relative, which is used in the following examples. This uncertainty may be somewhat higher close to the detection limit or in certain specific alloys (e.g. hypereutectic alloys). The uncertainty of 3% chosen for the examples is not intended to represent the uncertainties for all laboratories. In some instances it may be possible for individual laboratories to operate at a lower level of uncertainty.

Example 1 – Alloy with specified composition limits wide enough for effective use of guard bands

Consider an alloy having specified composition limits of 4.0 % to 5.0 % with a mid-point composition of 4.5 %. It is expected that the Spark-AES uncertainty from repeated analysis of the control material and sampling effects is as much as 3 % relative. Calculations based on 3 % uncertainty result in guard bands of 0.135 % (i.e. 0.03 * 4.5 %) and internal operating limits of 4.135 % (i.e. 4.0 % + 0.135 %) and 4.865 % (i.e. 5.0 % - 0.135 %). These limits define the operating range and would protect against false negative and false positive results, ensuring that the product complies with the specified composition limits.

The operating range with these internal operating limits is ± 8 % relative around the mid-point composition of 4.5 % (i.e. ± (100 * (4.865 - 4.135) / 4.5) / 2), which is a large enough window for the combination of furnace composition variability and analysis uncertainty.   In this case, the use of guard bands is possible.

Example 2 – Alloy with specified composition limits too narrow for effective use of guard bands

Consider an alloy having more narrow specified composition limits of 4.2 % to 4.8 % with a mid-point composition of 4.5 %. Again, calculations based on 3 % relative uncertainty yield guard bands of 0.135 % (i.e. 0.03 * 4.5 %) and internal operating limits of 4.335 % (i.e. 4.2 % + 0.135 %) and 4.665 % (i.e. 4.8 % - 0.135 %). These limits define the operating range and would protect against false negative and false positive results ensuring that the product complies with the specified composition limits. However, because of analysis uncertainty of ± 3 %, an alloy

sample having an actual composition of 4.5 % may yield analysis results between 4.365 % and 4.635 %, which consumes nearly the entire operating range of 4.335 % to 4.665 %.

The operating range with these internal operating limits is ± 3.7 % relative around the target composition 4.5 % (i.e. ± (100 * (4.665 – 4.335) / 4.5) / 2), which is a very narrow window for the combination of furnace composition variability and analysis variability. As a result, the use of guard bands would not be possible.

This discussion shows the importance of having specified composition limits that are wide enough to accommodate producer guard bands based on the expected uncertainty of measurement process while allowing for an adequate window for furnace composition variability. Customers should work with their suppliers to establish practical composition limits.

The above examples focus on potential risk of a supplier shipping off-composition product for a single element. However, the probability of shipping off-composition product can significantly increase when analyzing for multiple elements, if guard bands based on analysis uncertainty are not used.

Figures 6 and 7 illustrate the probability that out of specification product will be shipped as a function of the number of elements with guard bands varying from 0 % to 5 % relative difference from specified composition limits. The y-axis in Figure 6 has been expanded in Figure 7 to show the probability of shipping off-composition product when the guard bands are between 3 % and 5 %. The values plotted in Figures 6 and 7 have been calculated using two standard deviations equaling 3 % relative uncertainty in analysis.

Figures 6 and 7 highlight the beneficial use of guard bands by showing that the probability for an alloy to be off-composition decreases as the magnitudes of the guard bands increase, especially when multiple elements are considered. For example, the curve for a guard band of 0 % magnitude (i.e. no guard band) in Figure 6 shows that there is a 50 % probability the alloy will be outside the specified composition limits when the measured composition of an individual element is at the specified composition limit. With the same guard band of 0 % magnitude, the probability that the alloy will be outside the specified composition limits increases to 75 % when the measured compositions of two individual elements are at the specified composition limits. As the measured compositions of more elements are at the specified composition limits, the probability that the alloy will be outside the specified composition limits increases exponentially.

Risk of Shipping Off-Composition Material as a Function of Guard Band Magnitude when One or More Elements are at Specification Limits
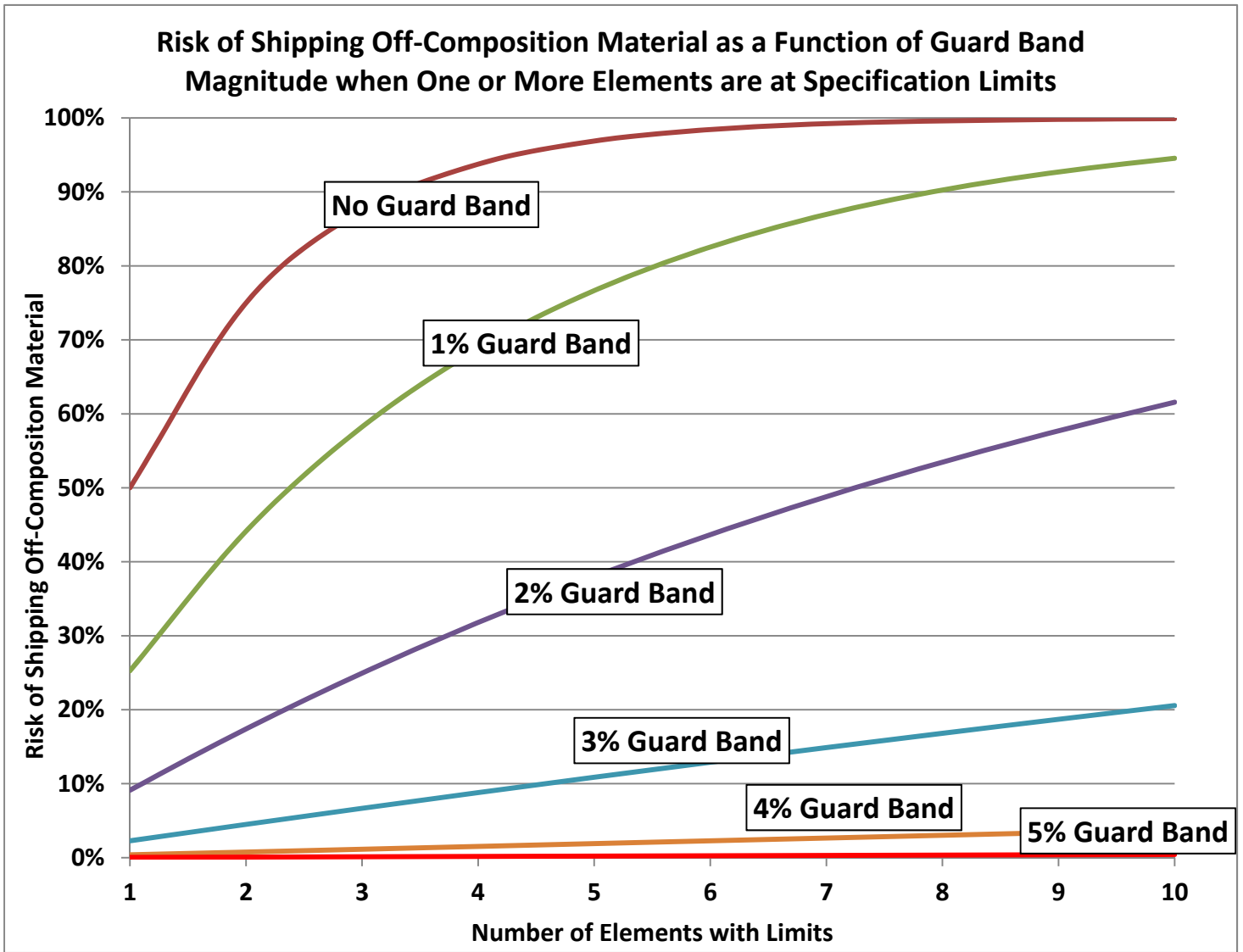
Figure 6. Probability a cast is off-composition for product with guard bands between 0 % and 5 % of the nominal concentration for a sample assuming a 3 % relative uncertainty in analysis.
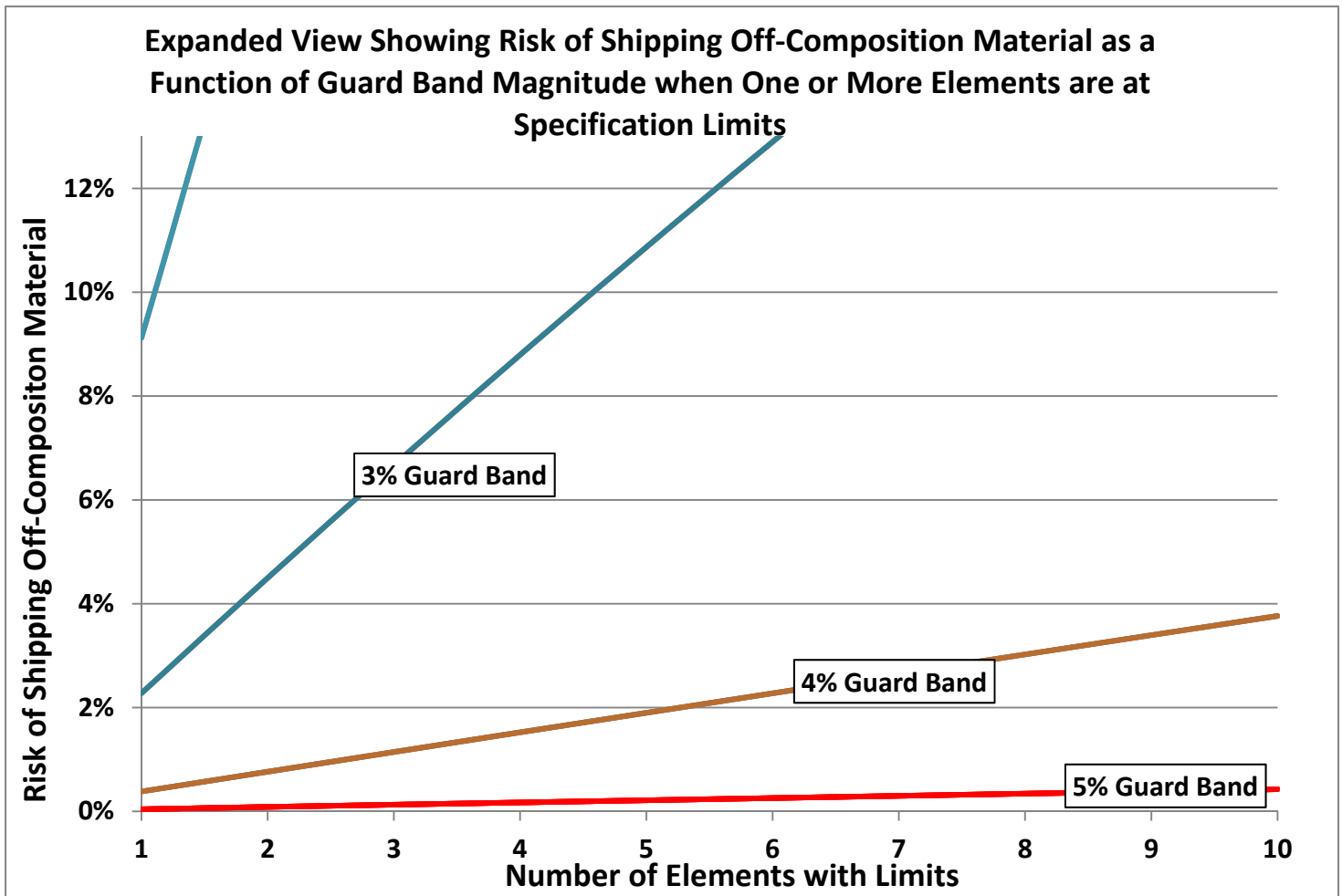
Figure 7. Expanded scale - Probability a cast is off-composition for product with guard bands between 3 % and 5 % of the nominal concentration for a sample assuming a 3 % relative uncertainty in analysis.

Significant digits

Spark-AES instruments can generate composition results with many more decimal places than are meaningful based on the uncertainty of the measurement. As a result, consideration should be given to the numbers of significant digits both requested and reported. To comply with ASTM E1251 (2), alloy compositions shall not be reported with more significant digits or higher precision than that of the certified reference material(s) used to calibrate or type standardize the spectrometer.

A good guideline regarding the certification of aluminum alloys is to report composition results using the number of decimal places specified by The Aluminum Association registration records

and ANSI standards (6, 7, 8, 9). The standards established by the Aluminum Association can generally be met with commercially available certified reference materials typically used for the control of spectrometers.

Trace Elements

Most of the discussion above focused on uncertainty in the analysis of alloying elements that are intentionally added. Specifications also typically include maximum levels allowed for some trace elements that may be present naturally in the base metal, in the alloying materials, or unintentionally introduced during the melting and casting processes. Two factors must be considered before requesting or accepting a specification for a trace level element: 1) the ability of the Spark-AES test method to quantify the element at the mass fraction in the specification, and 2) the availability of reference materials with values and uncertainties that are suitable for the maximum level in the specification.

Spark-AES instrument manufacturers typically report instrument detection limits for most elements in advertising literature and in documentation supplied with new instrumentation. Such estimates of instrument detection limits are made either under ideal conditions using high-purity aluminum or from the calibration model. In either case, the resulting estimate of the instrument detection limit is normally much lower than the method detection limit estimated using a standard test method developed for the analysis of aluminum alloys. This method detection limit estimation includes corrections for spectral and inter-element interferences, background signal shift, metallurgical structure, and material homogeneity.

Neither the instrument nor the method detection limit should be used to establish specification limits for trace elements. The method detection limit determines whether an element can be reported as present. The quantification limit determines whether a numerical value can be reported for the element. The quantification limit typically is 3 to 5 times the method detection limit. The maximum specification limit for a trace element should be set at some factor above quantification limit to accommodate analysis and reference material uncertainty.

In addition, reference materials of aluminum influence the lower limit of the calibrated analytical range. Values for trace elements in reference materials normally have uncertainty estimates up to 100 times greater than the instrument manufacturer's estimated detection limit.

Performance data based on actual analysis of trace elements in aluminum alloys by expert labs in the industry can be found in the inter-lab study included in ASTM E1251 (Standard Test Method for Analysis of Aluminum and Aluminum Alloys by Spark Atomic Emission Spectrometry). ASTM E1251 (2) also recommends against analysis of mercury (Hg) in Aluminum by Spark-AES.

The main sources of uncertainty of Spark-AES and their potential causes.

Uncertainty in elemental analysis, as in any analytical method, arises from systematic errors that introduce a bias in the analysis and random errors arising from small variations from a number of sources. The following discussion assumes systematic errors have been minimized by adherence to appropriate practices as defined in ASTM methods E716 and E1251, vendor recommended analysis practices, and the use as calibrants of reference materials composition similar to the alloys being analyzed.

Random error appears as variability in the measurement process. The variability may be observed in the short term as "spark-to-spark" or sample-to-sample variations, or in the longer term, as observed in a control chart of the average analysis result on a control sample plotted as a function of time.
Random errors in elemental analysis can be categorized according to the underlying cause of the error. A brief discussion of sample and sampling errors along with a Table summarizing other common sources of uncertainty follows.

<u>**Sampling and Sample Errors**</u>

Sampling and sample related errors tend to dominate the overall analysis uncertainty. Typically repeatability between sparks on a sample is 1.5 to 2 times higher than on a certified reference material of the same alloy. Poor sampling and/or sample preparation practices can lead to erroneous analyses and therefore wrong conclusions and/or decisions about conformance to specification or process adjustments (furnace corrections). The uncertainty due to sampling and sample related errors can be reduced by taking multiple samples and/or increasing the number of sparks used to determine the average result.

Sampling errors include factors such as:
- insufficient number of samples
- lack of homogeneity in the metal being sampled
- slow or non-continuous pouring (double pour)
- more than one sample poured out of the same ladle of metal
- mold not completely filled (sample and/or sprue not completely formed)
- contaminated metal, sampler or ladle
- improper sampler
- improper care of the sampler or ladle
- segregation related to the sample cooling rate and its directionality
- taking a sample with a cold mold
- taking sample when metal temperature in the furnace or trough is too low for a particular alloy
- allowing the metal in the ladle to cool excessively before pouring the sample

- removing the sample or breaking the sprue before complete solidification
- inclusions, skim or bath in the sample (observed before or after machining)
- porosity, cracks, voids or pits in the sample (observed before or after machining)
- rounded corners on the sample

Sample preparation errors include:

- incorrect or uneven depth of cut
- surface too rough or too smooth relative to an ideal surface of 63 microinches RMS (1.6 micrometers) sample and standard surfaces have different surface roughness
- samples not prepared properly using a milling machine or a lathe. Note: sanding or grinding may introduce contamination on the surface, tend to smear softer aluminum material over harder intermetallic particles, or eject harder intermetallic particles from the sample.
- contamination from coolant (if used)
- contamination from cutting tooling
- contamination from sample handling

Other sources of uncertainty

Other sources of uncertainty can be attributed to the method, the instrument or the surrounding environment and are covered in details in Appendix A.

Conclusions

Uncertainty in measurements is unavoidable. Numerous sources of errors, including but not limited to sampling, lab practices, and reference material uncertainty, are inherent in the analytical process used to certify the compositions of aluminum and aluminum alloys. When determining specified composition limits for a new product, or certifying the composition of an existing product against specified composition limits, it is recommended that guard bands are used to set internal operating limits to accommodate analysis uncertainty. Internal operating limits are an essential practice for producers to ensure compliance of product within specified composition limits.

Appendix A - Typical Sources of Uncertainty for Spark-AES analysis of Aluminum and Aluminum Alloys

Source of Uncertainty	Systematic error	Random error	Potential causes:
Calibration	x		• Inappropriate calibration model • Too few calibrants • Calibrant(s) with inadequate composition • Calibrant(s) with inaccurate or inhomogeneous composition • Calibration beyond instrument capability range • Extrapolation beyond element calibration range.
Spectral interferences and matrix effects	x	x	• Instrument configuration not suitable for analysis requirement • Incorrect inter-element correction models • Too few calibrants for setting correction models • Calibrant(s) with inadequate composition • Calibrant(s) with inaccurate or inhomogeneous composition
Standardization (Drift Correction)	x	x	• Incorrect selection of high (slope) and low (offset) drift correction standard samples • Only one drift correction standard sample for a particular element • Inhomogeneous drift correction standard sample • Magnitude of the slope and/or offset drift correction factors too high • Insufficient frequency of standardization • Insufficient number of sparks • Extrapolation beyond element calibration range • Calibrant inaccurate composition • Improper replacement procedure for implementing new drift correct standards • Contaminated analytical surface (finger print, coolant, air)

Type standardization	x	x	• Type standard with composition or metallurgical history not similar to production sample(s) • Extrapolation beyond element calibration range • Type standard with inaccurate composition • Incorrect selection of slope or offset type standardization factor • Inhomogeneous type standard sample • Magnitude of the slope and/or offset correction factors too high • Insufficient frequency of type standardization • Insufficient number of sparks • Contaminated analytical surface (finger print, coolant, air) •
Control sample analysis		x	• Control sample with composition or metallurgical history not similar to production sample(s) • Inhomogeneous control sample • Insufficient frequency of analysis • Absence of corrective action following an out of control result • Control sample limits too wide or too narrow • Insufficient number of sparks • Contaminated analytical surface (finger print, coolant, air)
Production sample analysis	x	x	• Sample composition outside element calibration range • Insufficient number of sparks • Air infiltration between instrument stand and sample • Spark overlap • Electrode not properly cleaned • Sparks outside the recommended spark radius as depicted in ASTM E-716 • Corrective action not taken when control sample analysis outside control limits • Contaminated analytical surface (finger print, coolant, air)
Instrument	x	x	• Temperature stability of instrument • Optical slit profile adjustment • Cleanliness of sample stand and argon supply

			line
			• Argon quality
			• Electrode positioning adjustment
			• Lens cleanliness
Laboratory environment	x	x	• Room temperature fluctuations
			• Humidity fluctuations
			• Line voltage fluctuations

Note: the list of sources of uncertainty was developed with the understanding that sample and reference material preparation conform to ASTM E716, and instrument operation and analysis practices conform to ASTM E1251.